

# Hyperpolarization Natural Abundance $^{17}\text{O}$ NMR Probes the Acidity Strength of Solid Catalysts

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Most consumer goods are manufactured from a range of basic chemicals and plastics, and are produced by the oil and petrochemical industries which heavily rely on heterogeneous catalytic processes involving solid acid catalysts.<sup>[1]</sup> The acidity strength of these catalysts are a critical factor controlling activity and selectivity. The OH bond length of the Brønsted acid site Si-O(H)-Al is directly related to the strength of the acidity, however experimentally accessing this distance by diffraction is challenging. Hydrogen atoms scatter x-ray radiation weakly and single crystal neutron diffraction is not accessible on these often amorphous phases.

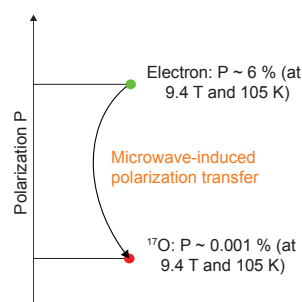
Over the years, a range of chemical, physicochemical and spectroscopic techniques have been developed to understand the nature of the acid sites and provide atomic scale characterization. In particular, solid-state Nuclear Magnetic Resonance (NMR) spectroscopy has played a very important role in increasing our understanding of the nature of acid sites.<sup>[2]</sup> For example, a qualitative empirical correlation exists between the acid strength of a Brønsted acid site and the  $^1\text{H}$  NMR chemical shift of the corresponding hydroxyls OH.

An alternative qualitative NMR approach consists of probing the oxygens of the hydroxyl environments. The spectra of  $^{17}\text{O}$ , which has a non-zero nuclear spin quantum number ( $I = 5/2$ ) and is the only NMR-active isotope of oxygen, are strongly dependent on chemical shifts and line widths, enabling a range of Brønsted acid sites to be probed. Additionally, their strengths are related to the dissociative ability of proton and therefore, in the case of solid acids, to the length of the OH bond  $r_{\text{OH}}$  which in solid state NMR is usually accessed by measuring the heteronuclear dipolar coupling between the nuclei.

However, the very poor natural abundance of  $^{17}\text{O}$  (i.e. 0.037 %) usually hinders its detection and therefore prevents both  $^{17}\text{O}$  NMR spectra and  $^1\text{H}$   $^{17}\text{O}$  dipolar coupling  $R_{\text{OH}}$  to be obtained. A synthetic pathway involving a limited number of  $^{17}\text{O}$  isotopically labelled sources (i.e.  $^{17}\text{O}_2$  and  $\text{H}_2^{17}\text{O}$ ) can be designed,<sup>[3]</sup> nevertheless, this strategy cannot constitute a general approach due to the need for the (often) expensive additional chemical synthesis procedure required and/or alteration of the chemical systems of interest.

The sensitivity of NMR experiments has always been a critical issue but has also repeatedly benefitted strongly from advance in both technology, such as higher magnetic field, cryoprobe and magic angle spinning, and methodology (e.g. Fourier transform, cross polarization) in order to always push the

limit of detection further. In particular, dynamic nuclear polarization (DNP), which belongs to a wider range of hyperpolarization techniques enabling large nuclear polarization beyond the Boltzmann distribution to be obtained, currently offers the most dramatic approach for NMR signal enhancement of multiple orders of magnitude.<sup>[4,5]</sup> This is achieved by a microwave-driven transfer of the high thermal electron polarization of unpaired electron spins (i.e. radicals or ions) to the weak nuclear spins before detecting the largely enhanced NMR signals (Figure 1). This strategy has been transformative in a range of physical and biological sciences systems, effectively enabling accelerated atomic scale structure determination without the need for isotopic labelling in NMR active nuclei.<sup>[4,5]</sup>



**Figure 1.** Schematic representation of the DNP process and microwave-induced electron nuclei polarization transfer. The polarization  $P$  calculated as  $\sim (\gamma h B_0)/(4\pi k_B T)$  is given at  $B_0 = 9.4$  T and  $T = 105$  K.

An exciting and natural application of DNP is therefore the fast observation of NMR signals arising from systems that are usually beyond the detection limit. This for example includes the studies of dilute species and molecules adsorbed on surfaces,<sup>[6]</sup> an approach called Surface-Enhanced NMR Spectroscopy (SENS). Poorly abundant nuclei also largely benefit from such an approach and it was recently demonstrated that DNP permits the fast detection of  $^{17}\text{O}$  at natural abundance,<sup>[7]</sup> paving the way to investigate oxide surfaces and subsurfaces.<sup>[8]</sup>

Being able to quickly, quantitatively and accurately probe Brønsted surface acidity at the atomic level remains a profound challenge. In a recent Communication in *Angewandte Chemie*, Perras, Pruski, and co-workers elegantly deploy natural abundance  $^{17}\text{O}$  SENS to observe a range of hydroxyl groups and report the precise determination of the OH bond lengths on a series of amorphous solid acids. Importantly, the authors also showed that these distances correlate well with the previously established potentiometric titration method to measure solid acidity which is based on the zero point of charge pH.

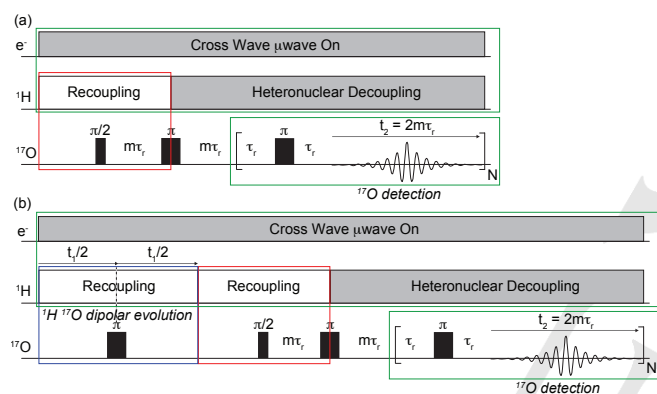
Overcoming the challenging poor sensitivity of  $^{17}\text{O}$  was achieved combining DNP with a powerful data acquisition strategy (Figure 2) to yield high signal to noise ratio  $^{17}\text{O}$  NMR spectra of mesoporous silica and a range of silica-alumina materials with different ratio at a magnetic field of 9.4 T. All the

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## HIGHLIGHT

NMR data acquisition involves an  $^1\text{H}$  and  $^{17}\text{O}$  heteronuclear polarization transfer step based on the Phase-shifted Recoupling Effects of a Smooth Transfer of Order (PRESTO) sequence<sup>[8,9]</sup> to selectively discriminate the hydroxyls from the other non-protonated oxygens. The extra sensitivity afforded by DNP<sup>[10]</sup> was not explicitly mentioned by the authors, nevertheless its combination with the detection of the free induction decay (fid) during a train of refocusing  $\pi$  pulses obtained with the Quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) experiment (Figure 2a) under Magic Angle Spinning (MAS), and making use of the much longer transverse relaxation time  $T_2^*$  than the magnetization dephasing time  $T_2^*$ , yields natural abundance  $^{17}\text{O}$  NMR spectra. These spectra are presented as series of finite number of discrete spin-echo sidebands or 'spikelets' obtained after Fourier transformation (FT) of the fid and leads to a considerable increase in sensitivity. The manifold of these rotatory sidebands reproduces the standard looking frequency-domain NMR lineshape which can also be obtained by summing the rotational echoes followed by FT.



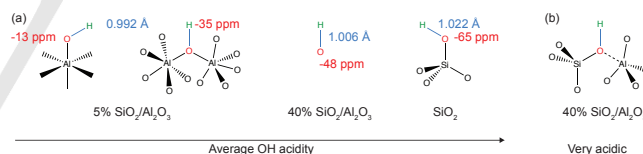
**Figure 2.** Data acquisition strategy for recording natural abundance  $^{17}\text{O}$  SENS NMR data: schematic representation of the pulse sequence for (a) acquiring  $^{17}\text{O}$  NMR spectra and (b) probing  $^1\text{H}$   $^{17}\text{O}$  heteronuclear dipolar coupling  $R_{\text{OH}}$ , using signal enhancements techniques (DNP, Heteronuclear Decoupling, green box),  $^1\text{H}$   $^{17}\text{O}$  heteronuclear polarization transfer (PRESTO, red box) and proton-detected local field spectroscopy (PDLF, blue box).<sup>[11]</sup> The location of the  $^{17}\text{O}$  NMR detection and  $^1\text{H}$   $^{17}\text{O}$  dipolar evolution are given in italics. Recoupling sequences used are based on the symmetry rules.<sup>[12]</sup> m and N are integers and  $\tau_r$  the rotor periods.

A range of silanols (Si-OH), bridging (Al-O(H)-E, E = Si or Al) and non-bridging aluminols (Al-OH) (Figure 3a) were observed on the solid acids investigated. The large quadrupolar coupling of these different oxygens (i.e. 6.6 MHz for Al-(OH)-Si in related zeolite HX)<sup>[2]</sup> prevents their resolution at 9.4 T, however the spectral assignment was based on their known shifts from the literature, the  $^{17}\text{O}$  shifts decreasing with the anticipated larger  $^{17}\text{O}$  shieldings of stronger Brønsted acids. The width of the  $^{17}\text{O}$  DNP SENS spectra observed also reflects the distribution of the hydroxyl sites as relatively narrower lines are detected for the mesoporous silica and the 5%  $\text{SiO}_2/\text{Al}_2\text{O}_3$  sample due to the majority of Si-OH and Al-OH/Al-O(H)-Al oxygens present, respectively. A broader  $^{17}\text{O}$  NMR spectrum is observed for the 40%  $\text{SiO}_2/\text{Al}_2\text{O}_3$  material which likely contains a range of bridging hydroxyls, and includes the Brønsted acid site Si-O(H)-Al (Figure

3b) which disappears upon deprotonation with pyridine.

The authors built upon this natural abundance  $^{17}\text{O}$  NMR detection approach to extend the work further and successfully probe the oscillation of the  $^{17}\text{O}$  NMR signal due to the strong  $^1\text{H}$   $^{17}\text{O}$  dipolar coupling  $R_{\text{OH}}$  using Proton-Detected Local Field (PDLF). This is accomplished by using the latest development in symmetry-based recoupling NMR pulse sequence,<sup>[12]</sup> as well as FT of the dipolar modulation to yield a simple doublet to precisely measure  $R_{\text{OH}}$  (Figure 2b). This approach is not dissimilar to the one used in high resolution liquid-state NMR spectroscopy to measure scalar J coupling constants and enables here the determination of the average OH distances in a range of hydroxyls to be obtained quickly, accurately and with sub-pm precision.

The fast quantification of OH bond length permits comparison between mesoporous silica and silica-alumina samples and large differences were observed as anticipated for these materials with widely different acid base and proton's lability properties. For example, it was found that the silanols Si-OH on silica have similar OH distance to that of the acid  $\text{CaH}_2\text{PO}_4$  ( $1.022 \pm 0.006 \text{ \AA}$  vs  $1.025 \pm 0.005 \text{ \AA}$ ) in agreement with the Brønsted acidity of this phase. In contrast, shorter bond lengths were obtained for the hydroxyls of 40%  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ( $1.006 \pm 0.009 \text{ \AA}$ ) and of 5%  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ( $0.992 \pm 0.004 \text{ \AA}$ ), the latter being mostly aluminols, these results being in line with the strong Lewis basicity of these sites. It is worth pointing that only the average OH bond length can be determined, resulting from the absence of sites resolution, therefore prevents the measurement of the anticipated long OH distance of the Brønsted acid site Si-O(H)-Al (Figure 3b). Nevertheless, using these data and the known zero point of charge pH for a range of solid acids, the authors confirmed the inverse correlation between the proton's lability and OH bond length.



**Figure 3.** (a) Silica-alumina and silica ranked according to their increasing average OH acidity along with some proposed hydroxyl environments. The structures of the terminal aluminols (Al-OH) and bridging aluminols (Al-O(H)-Al) are given from Boehmite. Their  $^{17}\text{O}$  center of masses and average OH distances are given in red and blue, respectively. (b) Proposed structure of the very acidic Brønsted silanols (Al-O(H)-Si) sites from recent work.<sup>[13]</sup>

In conclusion, the work of Perras, Pruski, and co-workers discussed in this Highlight has illustrated the enormous potential that exists in determining detailed atomic scale structural feature in heterogeneous catalysis by harnessing the large solid-state NMR signal enhancements obtained with DNP (along with other data acquisition strategies). The detection of the otherwise often invisible  $^{17}\text{O}$  spins at natural abundant demonstrates an approach permitting the observation of Brønsted acid sites and insights into their strengths for a range of amorphous solid acids.

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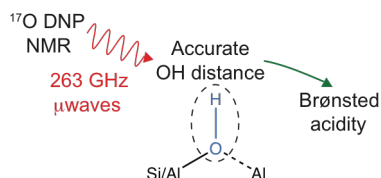
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## HIGHLIGHT

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By enhancing the solid-state nuclear magnetic resonance signals of  $^{17}\text{O}$  at natural abundance with dynamic nuclear polarization, Perras, Pruski *et al.* were able to measure oxygen – proton distances very accurately with sub-pm precision. The results enable insight into the Brønsted acidity on a range of solid acid catalysts to be obtained efficiently.



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